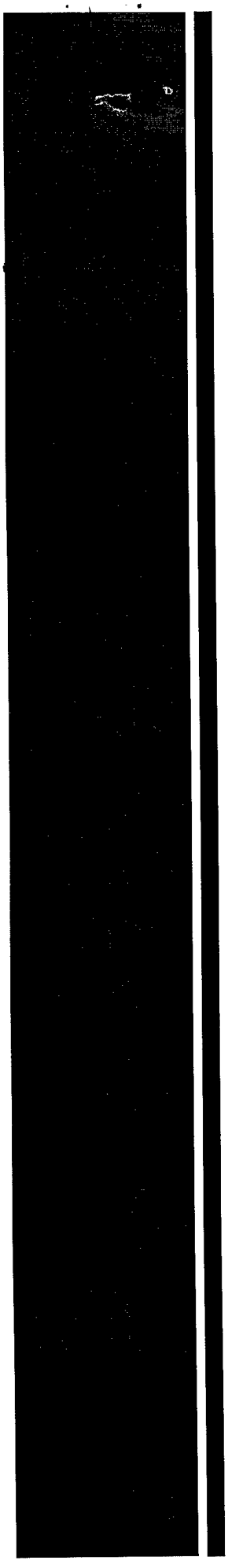

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On-Site Method for Measuring Nitroaromatic and Nitramine Explosives in Soil and Groundwater Using GC-NPD

Feasibility Study

Alan D. Hewitt and Thomas F. Jenkins

August 1999

Abstract: An on-site method has been developed for estimating concentrations of TNT, RDX, 2,4-DNT, and the two most commonly encountered environmental transformation products of TNT, 2-amino-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene, in soil and groundwater using gas chromatography and the nitrogen-phosphorus detector (NPD). Soil samples (20 g) are extracted by shaking with 20 mL of acetone, and extracts are filtered through a Millex SR (0.5-μm) filter. Groundwater samples (1 L) were passed through SDB-RPS extraction disks that were subsequently extracted with 5 mL of acetone. A 1-μL volume of a soil or water extract is manually injected into a field-transportable gas chromatograph equipped with a NPD and a heated injection port. Separations are conducted on a Restek Crossbond 100% dimethyl polysiloxane column, 6 m × 0.53-mm i.d., 1.5 mm, using nitrogen carrier gas at 9.5 mL/min. Retention times range from 3.0 min. for 2,4-dinitrotoluene (2,4-DNT) to 5.6 min. for 2-amino-4,6-dinitrotoluene. Method detection limits were less than 0.16 mg/kg for soil and less than 1.0 μg/L for groundwater. One of the major advantages of this method, over currently available colorimetric and enzyme immunoassay on-site methods, is the ability to quantify individual target analytes that often coexist in soils and groundwater contaminated with explosive residues. This method will be particularly useful at military antitank firing ranges where it is necessary to quantify residual concentrations of RDX in the presence of high concentrations of HMX, and when the transformation products of TNT need to be identified.

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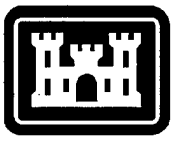

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Prepared for
OFFICE OF THE CHIEF OF ENGINEERS
and
U.S. ARMY ENVIRONMENTAL CENTER
SFIM-AEC-ET-CR-99044

PREFACE

This report was prepared by Alan D. Hewitt, Research Physical Scientist, and Dr. Thomas F. Jenkins, Research Chemist, Geological Sciences Division, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire.

Funding for this work was provided by the U.S. Army Environmental Center, Martin H. Stutz, Project Monitor, and from the U.S. Army Corps of Engineers Installation Restoration Program, Work Unit AF25-CT-006, Dr. M. John Cullinane, Program Manager. The authors thank Dr. C.L. Grant and Dr. P.H. Miyares for technical review of the text.

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Feasibility Study

ALAN D. HEWITT AND THOMAS F. JENKINS

INTRODUCTION

Until the last several years, almost all sites potentially contaminated with toxic and hazardous wastes were characterized by shipping soil and water samples to off-site laboratories for analysis. These off-site laboratories utilized powerful laboratory instrumentation and followed methods such as those that have been standardized through the U.S. Environmental Protection Agency's SW846 Methods compendium. In general the data obtained in this way were adequate to make decisions on whether sites were contaminated at levels that required remedial activities. Action levels for explosives, although not universally accepted, have generally been based on water quality criteria. The interim EPA guidance indicates that concentrations as low as 2 μg/L for 2,4,6-trinitrotoluene (TNT) may have some level of human toxicity (U.S. EPA 1989). Action levels for soil have generally been in the milligram/kilogram range.

A major downside of this approach is the time involved in producing the data for making these decisions. It often takes weeks to months after samples were collected before data become available to project personnel. Secondly, this approach was extremely expensive on a per sample basis, resulting in the analysis of a relatively few samples to characterize large geographical areas. Recognition of these problems led to the development of analytical methods that could be used on site to provide adequate characterization when rapid decisions were required. Because of lower analysis costs, these methods allowed more samples to be analyzed resulting in a more spatially detailed characterization.

The first on-site method for detecting explosives residues in water was reported by Heller et al. (1982) and later improved by Erickson et al. (1984), who extended its application to include soils. This method was specifically aimed at the detection of TNT and utilized a detection tube that had two sections. The first section contains a basic oxide that converts TNT to its Meisenheimer anion. This colored species migrates to the second section of the tube, where it is retained on a quaternary ammonium chloride ion exchange resin. Water samples were pumped through this tube, and TNT was detected visually by the development of a reddish stain on the second section of the tube. The concentration of TNT was estimated from the length of the stain produced. Soil samples are first extracted with methanol, and then this solvent is passed through the tube. The tubes have been independently evaluated at CRREL and found to provide reliable detection of the presence of TNT at concentrations greater than 40 μg/L, but the ability to precisely and accurately quantify TNT concentrations in water or soil was poor (Jenkins and Schumacher 1990). Moreover, the 1-minute extraction time specified for soil was insufficient for field samples.

Stevanovic and Mitrovic (1990) developed a method for TNT and 1,3,5-hexahydro-1,3,5-trinitrotriazine (RDX) that could be adapted for on-site analysis. In this method, water is passed through a porous disk coated with a thin film of silica gel, and TNT and RDX are adsorbed on the

surface. The disk is dried and sprayed with a color forming solution of o-toluidine for TNT and Griess reagent for RDX. Measurement is made by reflectometry, and detection limits of about 200 µg/L were estimated.

Seitz and coworkers at the University of New Hampshire developed a fiber-optic-based approach for on-site measurement that utilizes the reaction of TNT with an amine-loaded poly(vinyl)chloride (PVC) membrane to form a colored product (Zhang et al. 1989, Zhang and Seitz 1989). This approach was specific for TNT, and has a detection limit of about 100 µg/L.

In another approach, TNT and RDX were absorbed into a cellulose acetate membrane containing pyrenebutyric acid, and concentrations were estimated via fluorescence quenching by the nitro groups (Jian and Seitz 1990). Detection limits were estimated at 2 and 10 mg/L.

A photometric method for RDX was developed by Hass and Stork (1989) and Hass et al. (1990) that involves evaporation of a 500-mL water sample to dryness, followed by reaction of the residue with diphenylamine in sulfuric acid. A colored product is produced and the concentration of RDX is estimated from the absorbance at 596 nm. The detection limit of about 5 µg/L is nearly adequate for this application, but the procedure is cumbersome and impractical for on-site use.

Colorimetric-based methods for TNT and RDX in water and soil were developed at CRREL (Jenkins 1990, Walsh and Jenkins 1991, Jenkins et al. 1994, Jenkins and Walsh 1998). Soil samples (20 g) are extracted with 100 mL of acetone. Water samples are passed through two solid-phase extraction membranes, and the retained compounds were eluted from each membrane with acetone. The acetone extract of the first membrane is reacted with a base, producing highly colored Janowsky anions. The acetone soil extracts are processed in an identical manner. The concentration of TNT is estimated from the absorbance measured with a field-portable spectrophotometer at 540 nm. The acetone extract of the second membrane or that from soil extraction is acidified and reacted with zinc powder to convert RDX to nitrous acid. The solution is filtered and further reacted with a Griess reagent to produce a highly colored azo dye. RDX concentration is estimated from the absorbance measured at 510 nm. Detection limits for TNT and RDX using these colorimetric methods were 1 µg/L and 4 µg/L, in water, respectively, and 1.0 and 1.4 mg/kg for soil. These methods have been available commercially from EnSys (now Strategic Diagnostics) for several years and have been widely used.

Keuchel et al. (1992a,b and 1994) was the first to report on the development of an enzyme immunoassay (EIA) method for TNT in water and soil. Commercial test kits for TNT using EIA were first introduced by Strategic Diagnostics Corporation (SDI) in 1993 (Hutter et al. 1993). Subsequently, SDI produced a commercial EIA method for RDX as well (Teaney and Hudak 1994). These methods are known commercially as the D TECH™ EIA methods. Detection limits for TNT and RDX in water using the D TECH were reported as 5 µg/L. Detection limits for soil were 0.5 mg/kg for both TNT and RDX. Along with the colorimetric methods, the D TECH methods have been used extensively in the past several years for on-site determination of TNT and RDX in groundwater and soil.

The U.S. Naval Research Laboratory (NRL) has developed a continuous flow immunosensor (CFI) for on-site determination of TNT and RDX in water (Bart et al. 1997). This method is an extension of the EIA methods and uses either TNT or RDX antibodies that are immobilized on a membrane saturated with a fluorescent-labeled antigen. An aqueous buffer is pumped across the membrane and samples are injected into the flowing buffer. If the appropriate analyte is present, binding occurs with the membrane, thereby releasing the labeled antigen that is detected using a fluorometer. Detection limits appear to be about 10 µg/L using this system.

Another approach for on-site determination of TNT and RDX, developed at NRL, is the fiber optic biosensor (Shriver-Lake et al. 1995, 1997). These are also EIA-based methods. For TNT, fluorescent-labeled trinitrobenzene (TNB) is exposed to an antibody-coated optical fiber, producing a reference signal. When the fiber is then placed in a solution containing TNT, the signal is reduced as TNT competes for sites on the fiber. The reduction in signal is used to estimate TNT concentration. Estimates of RDX concentrations are obtained similarly. Detection limits for this method have been estimated at 10 µg/L.

DEFICIENCIES WITH CURRENT METHODS AND OBJECTIVES OF THIS STUDY

A summary of the performance characteristics of the various on-site methods for TNT and RDX in soil is presented by Crockett et al. (1996, 1998), and the performance characteristics in groundwa-

ter are summarized by Crockett et al. (in press). Currently available on-site methods for explosives residues in water and soil generally can inexpensively provide reliable estimates for the concentrations of TNT and RDX. To our knowledge no on-site methods for explosives analytes other than TNT or RDX have been reported except colorimetric-based methods for 2,4 DNT (Jenkins and Walsh 1992) and ammonium picrate (Thorne and Jenkins 1995); the RDX colorimetric method has been used to estimate octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) concentrations at antitank firing ranges where the concentration of HMX was several orders of magnitude higher than that of RDX (Jenkins et al. 1997, 1998). Therefore, no on-site methods currently provide comprehensive data for the suite of other manufacturing impurities and environmental transformation products that are often present at explosives-contaminated sites (Walsh et al. 1993). In addition, for antitank ranges, neither colorimetric nor immunoassay-based methods are capable of estimating concentrations of RDX when HMX is present at equal or higher concentrations (Jenkins et al. 1998). Similarly, the concentration of TNT cannot be estimated accurately using these methods when DNT, TNB or 2,4,6- trinitrophenylnitramine (tetryl) is present. Moreover, no currently available on-site method provides for the determination of the major biotransformation products of TNT, 4-amino-2,6-dinitrotoluene (4ADNT) and 2-amino-4,6-dinitrotoluene (2ADNT), which are sometimes present at higher concentrations than TNT itself (Jenkins et al. 1998). Thus there is a need for an on-site analytical method that can provide simultaneous estimates of the entire suite of analytes that are commonly present at explosives-contaminated sites.

Gas chromatography has been used extensively for many years in on-site methods to identify and quantify specific target chemicals associated with fuels and solvents (U.S. EPA 1997). The availability of the nitrogen-phosphorus detector (NPD) and the electron capture detector (ECD) on field transportable instruments provides selective detectors for nitrogen containing organic compounds and electron deficient compounds, respectively. Both detectors are selective and sensitive for the most commonly encountered explosives such as TNT, RDX and tetryl, as well as their manufacturing impurities and environmental transformation products. Recently, Walsh and Ranney (1998) demonstrated that gas chromatography with a fused silica macrobore column (0.53 mm) provides adequate separation for the suite of analytes commonly encountered at explosives-contaminated sites. Gas chromatography has not received wide use for these analytes because of their thermal instability, but this analysis is possible by using a deactivated injection port and setting high linear velocities for the carrier gas with short fused silica macrobore columns.

It was the intent of this work to evaluate the potential for using a field-transportable gas chromatograph (GC) equipped with NP and EC detectors for on-site determination of individual explosives-related analytes. In particular an emphasis was placed on the ability to determine (1) RDX in the presence of HMX for use at antitank firing ranges, (2) the biotransformation products of TNT, which are 2ADNT and 4ADNT, and (3) simultaneous estimates for the suite of analytes commonly encountered at explosive-contaminated sites, since no currently available on-site method can perform these three tasks.

EXPERIMENTAL METHODS

Calibration standards

Analytical standards of 2,4-dinitrotoluene (2,4-DNT), TNT, RDX, 4ADNT, 2ADNT, and HMX were prepared from standard analytical reference materials (SARMs) obtained from the U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland. A primary stock standard of approximately 1000 mg/L for each analyte was prepared by transferring a weighed amount into acetone and diluting to 100 mL in a glass volumetric flask. Combined analyte secondary stock standards ranging from approximately 0.25 to 200 mg/L were prepared by transferring up to 1.00 mL of each primary stock standard with either glass syringes or glass pipettes into prepared bottles and volumetric flasks containing acetone. Both the primary and secondary stock standards were stored in a refrigerator at 4°C and removed only for brief periods while in use. Moreover, because of the instability of some of these compounds at low concentrations, working standards for the levels shown in Table 1 were prepared daily (Walsh and Ranney 1998). Henceforth 2,4-DNT, TNT, RDX, 4ADNT, and 2ADNT will be collectively called target analytes.

Instrumentation and separations

A field-transportable SRI model 8610 gas chromatograph, equipped with a heated on-column

Table 1. Concentration ranges for the working standards of TNT, 2,4-DNT, RDX, 2ADNT, and 4ADNT prepared for the evaluation of the nitrogen-phosphorus (NP) and electron capture (EC) detectors.

Detector	*Concentration range (mg/L)*
NPD	0.25–10.0
ECD	0.01–1.00

injector (8690-0025) and two detectors, a NPD (8690-0015) and ECD (8690-0020, Ni^{63}), was used for this study. Separations were performed on a Crossbond 100% dimethyl polysiloxane column, 6 m × 0.53 mm i.d., 1.5 µm (Restek MXT-1). The injection-port temperature was 250°C and the nitrogen carrier gas was set at about 9.5 mL/min (36–40 psi). Injections (1 µL) were made manually with a 10-µL glass syringe (Hamilton) equipped with an extra long needle (7.5 cm).

When the NPD detector was used, the oven temperature was initially held at 100°C for 2 min; then the temperature was programmed at 20°C per minute to 240°C, and held at 240°C for 0.5 minutes. Air from the onboard purification system was supplied at 6 psi (41 kPa) and zero grade hydrogen was supplied at 7 psi (48 kPa) (flow rate was approximately 2 mL/min). The voltage setting for the NPD was 350 V and this detector was unheated.

When the ECD was used, the nitrogen makeup gas was supplied at 36–40 psi (248–276 kPa) by splitting the flow from the carrier gas supply line. For ECD analyses the oven temperature was initially held at 140°C for 6 min, then temperature programmed at 20°C per minute to 180°C, while the detector was maintained at 250°C.

RP-HPLC analyses

Confirmation analyses, by reversed phase high performance (RP-HPLC), were performed on the working standards, stock aqueous solutions (used for the aqueous method detection limit [MDL] study), and field-contaminated soil samples. The acetone-based standards and soil extracts were diluted 1:5 (0.300 mL acetone + 1.200 mL water) with reagent-grade water prior to analysis. Confirmation analyses of the target analytes was conducted on a C-8 column, 15 cm × 3.9 mm (Nova Pak). The eluent was 85:15% water/isopropanol flowing at 1.4 mL/min. Retention times for the five target analytes were RDX—2.9 min., TNT—5.3 min, 2,4-DNT—10.3 min, 2ADNT—13.5 min, and 4ADNT—15.4 min. Determination of HMX was conducted using a 25-cm × 4.6-mm CN column (Supelco) using 50:50% water/methanol flowing at 1.4 mL/min. The retention time for HMX was 11.1 min.

Sample preparation—soil

All soils were obtained from near-surface locations and air dried. While transferring subsamples of soil to 40-mL amber VOA vials, pebbles larger than 2 mm in diameter or any large pieces of vegetation were excluded. For the MDL study we used an explosive-free soil obtained at Ft. Ord, California. All other field soils analyzed were removed from bulk samples in which detectable explosive residues had been identified. These field-contaminated samples had been obtained at firing ranges and ammunition production plants.

Soil samples were prepared for the MDL study by placing 20 g into seven separate amber 40-mL VOA vials. These samples were each spiked by adding 1.00 mL of an acetone solution containing the five target analytes and HMX, using a glass pipette. This volume of spiking solution wetted the top three-quarters of the soil and created a soil concentration of approximately 0.5 mg/kg, for each analyte. After standing uncovered for 1 hour inside an exhaust hood, 20 mL of acetone was transferred to each vessel using a graduated cylinder. Each bottle was capped and shaken several times over a 5-minute period. The suspended soil was allowed to settle for 30 minutes then a 3-mL aliquot of the supernatant was pulled into a 5-cm^3 Luer-Lok syringe (Becton Dickinson & Co.) while leaving a pocket of air between the plunger and solvent extract. The air pocket prevented the acetone extract from coming into contact with the rubber plunger, which could compromise the analysis. The extract was filtered through a Millex-SR 0.5-µm disposable filter unit (Millipore), discarding the first 1-mL portion and collecting the remainder into an amber 2-mL vial for subsequent instrumental analysis. Likewise, portions of eight field-contaminated soils were extracted with acetone and filtered in preparation for analysis.

Sample preparation—water

The MDL study for aqueous samples was performed using a 1-L volume of reagent-grade water fortified with the target analytes. An aqueous

spiking solution was prepared by combining the appropriate volumes of individual aqueous stock standards after verifying their concentrations by RP-HPLC analysis (Grant et al. 1993). One-milliliter aliquots of this solution were then diluted up to 1.00 L, to make seven 1-L water samples. The resulting analyte concentrations in these 1-L samples ranged from 2.08 to 2.71 µg/L. These samples were preconcentrated (200 fold) using membrane solid phase extraction (SPE, [Empore 3M, SDB-RPS, 47 mm]) and eluted with 5 mL of acetone, following the procedure outlined by Jenkins et al. (1994).

For this study an apparatus was used that consisted of three filtering funnels attached to a common manifold. The manifold allowed three samples to be prepared simultaneously and all the filtrate to be collected in a 2-L vacuum flask. Briefly, after rinsing the extraction funnels (Kontes), collection vessels, and tongs with acetone, 47-mm membrane disks was placed on each support screen and wetted with acetone before centering each funnel and clamping in place. Each membrane was precleaned with two 10-mL aliquots of acetone. Prior to the second aliquot being pulled completely through the membrane, a 30-mL aliquot of organic-free water was added to a funnel. Near the completion of filtering this aliquot of water, a second 30 mL aliquot was added. With a small volume remaining from the second water rinse, a 1-L fortified water sample was added to the funnel. A small vacuum was applied throughout these cleaning and rinsing cycles, then adjusted during a sample preconcentration step so that the solution passed through the membrane at approximately 100 mL/min. After the sample had completely passed through a membrane the vacuum remained on for an additional 10 minutes to help remove all of the water.

Once dried, the entire funnel and membrane support was removed from the manifold and water drops were removed from the tip of the drain tube with a clean acetone wetted towel. Before returning a funnel and membrane support to the manifold, a 25- × 200-mm test tube was positioned to collect any further solution passing through a membrane in the filter assembly. Then 5 mL of acetone was poured over the interior surface of a funnel and allowed to cover the membrane for three minutes before applying a small vacuum and slowly pulling through. The volume of acetone recovered during a membrane extraction step was 4.2 ± 0.2 mL.

Miscellaneous variables

For many soils, the use of acetone and vigorous agitation (hand shaking) results in near-quantitative recovery of explosive compounds within 3 minutes (Jenkins 1990, Walsh and Jenkins 1991). Noted exceptions, however, are heavy clays or high organic soils, which have demonstrated slow extraction kinetics. For this reason, extraction time for a given soil must be verified at each location (Jenkins and Walsh 1998). Initially, when developing field screening methodologies, a 20-g soil sample (undried) was extracted with 100 mL of acetone at a soil to solvent ratio 1:5, so as to ensure that the water content of the final extract was not too high for the colorimetric based methods of determination. Subsequent studies with this field screening method determined that the water content in the acetone extract was not an issue. Therefore, to maximize delectability in soil, a sample weight (g) to acetone volume (mL) ratio of 1:1 could be used.

Following the same logic, sample preparation for the on-site analyses of explosive residues by GC also used a 1:1 ratio. To assess if soil moisture would affect instrumental responses, solutions were prepared to simulate the extracts that would be obtained when a 1:1 ratio of sample weight to acetone volume was used with soils of 5, 10, 20, 30, 40, 50% moisture by dry weight. Furthermore, to assess the range of application of the method and potential use of non-reagent-grade acetone, the following experiments were performed to (1) determine the detectability and retention times of other common explosives, (2) estimate the upper limit of linearity for the target analytes, and (3) examine the feasibility of using hardware-store grade acetone for sample extraction. The additional explosives determined were nitrobenzene; ortho-, para-, and meta- nitrotoluene; 1,3-dinitrobenzene; 2,6-dinitrotoluene; 1,3,5-trinitrobenzene; and methyl-2,4,6-trinitrophenyl nitramine (tetryl). Acetone-based standards of these analytes were prepared from archived stock standards.

RESULTS AND DISCUSSION

GC separations

The GC and its configuration was selected based on the works of Walsh and Ranney (1998). Here, we strived to meet the following goals: easy field implementation, minimal consumable support, and rapid analysis time (less than 15 min.).

In the study by Walsh and Ranney (1998), they injected solvent extracts into the heated injection port of a Hewlett-Packard 5890 GC equipped with an ECD and a 6-m, 0.53-mm-i.d. polydimethylsiloxane column. They established that responses for analytes with low vapor pressures were enhanced by increasing the linear velocity of the carrier gas and the injection port temperature. Following their lead, we chose on-column injections into a heated injector and a carrier gas flow rate of 9.5 mL/min that produced a linear velocity of 70 cm/sec. The two detectors used different chromatographic conditions because, while temperature programming was feasible with the NPD, excessive baseline drift limited the ECD to isothermal operation during the elution of the target analytes.

Typical chromatograms of the target analytes for the NP and EC detectors, are shown in Figures 1 and 2, respectively. Analysis of samples with high concentration of HMX confirmed that the latest eluting peak(s) (retention time > 7.5 min) was indicative of this compound (Fig. 1). However, either the low vapor pressure of HMX caused it to rapidly condense once leaving the column, or it was thermally degraded, and consequently these late eluting peaks could only be used to qualitatively identify its presence. The GC manufacturer suggested that upgrading the NP detector to one with a heater would eliminate this quantitation problem. We have not yet verified this possibility. HMX was not detected by the ECD. Here a long metal transfer line exists between the column and detector, and HMX compound is known to be very reactive with hot metal surfaces (Walsh and Ranney 1998). More work is underway to find a way to include HMX determination in this method.

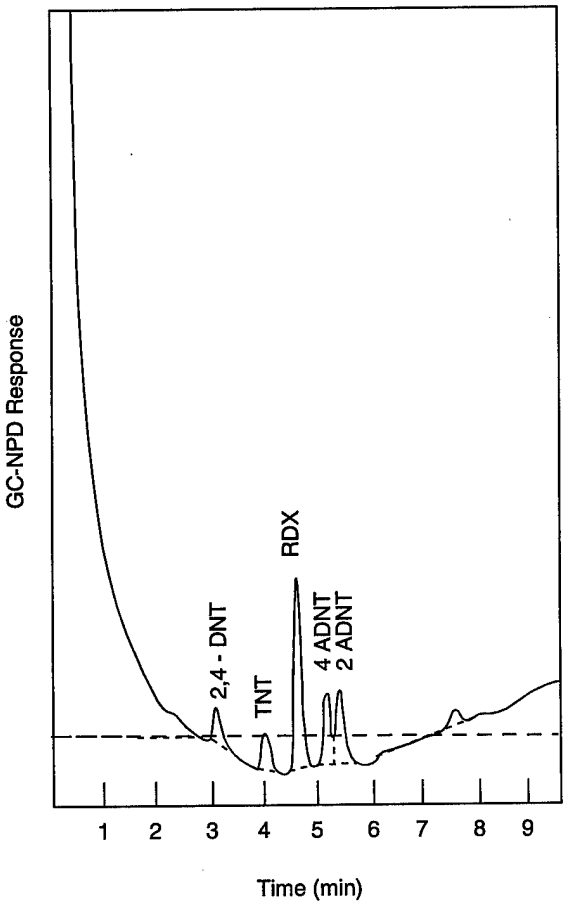

Figure 1. Chromatogram of 2,4-DNT, TNT, RDX, 4ADNT, 2ADNT, and HMX by GC-NPD analysis. Chromatogram is of one of the MDL samples (approximately 0.5 mg/kg).

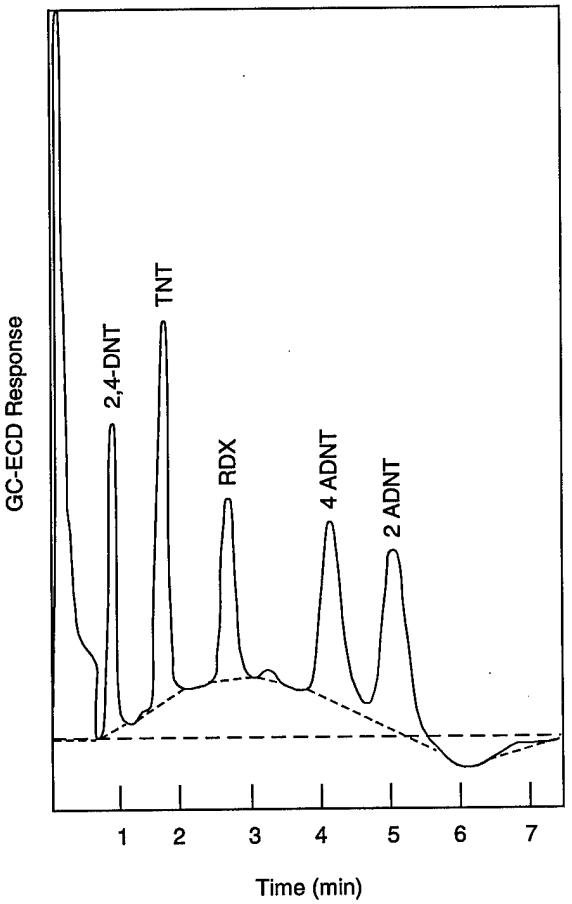

Figure 2. Chromatogram of 2,4-DNT, TNT, RDX, 4ADNT, and 2ADNT by GC-ECD analysis. Analyte concentrations approximately 0.5 mg/kg.

Table 2. Response factors for the GC-NPD, based on the average of triplicate measurements of both peak area and height.

A. Peak area response factors (SRI integrator peak area divided by mg/L concentration).

Concentration (mg/L)	Response factors ($\times 10^7$)				
	2,4-DNT	TNT	RDX	4ADNT	2ADNT
10	6.13	5.29	23.3	8.72	11.0
5	6.21	5.18	23.6	8.74	11.1
1	5.32	4.61	21.3	8.28	10.5
0.5	4.57	4.46	19.8	8.35	10.1
0.25	5.13	3.85	17.4	9.34	11.1

B. Peak height response factors (SRI integrator peak height divided by mg/L concentration).

Concentration (mg/L)	Response factors ($\times 10^6$)				
	2,4-DNT	TNT	RDX	4ADNT	2ADNT
10	5.67	5.51	24.5	9.45	10.1
5	6.04	5.35	25.1	9.67	10.3
1	5.60	4.77	22.7	9.08	9.55
0.5	5.18	4.43	20.0	8.70	8.69
0.25	4.94	3.82	18.0	9.03	9.19

Response factors

Tables 2 and 3 show the response factors obtained for the five target analytes on the NP and EC detectors, respectively, over the concentrations shown in Table 1. The response factors for the ECD systematically decreased with increasing concentration for all of the target analytes (Table 3) while the opposite trend, to smaller extent, was observed for the NPD for three of the five analytes (Table 2). To rule out the possibility that the slight increase in response factor seen for the NPD over this concentration range, which is unusual, was not due to incorrectly prepared standards, the standards were also analyzed by RP-HPLC. The response factors shown in Table 4 for RP-HPLC analysis failed to show any relationship to concentration, and resulted in much lower relative standard deviations (RSDs). The superior precision of RP-HPLC is due to a combination of variables: better sensitivity, an automated 100-µL sample injection volume, greater analyte peak symmetry, and better peak resolution. Figure 3 and 4 show the responses of these two detection systems to RDX. Because the response of the ECD is more nonlin-

Table 3. Response factors (SRI integrator peak height divided by mg/L concentration) for GC-EC detector, based on the average of duplicate meaurements.

Concentration (mg/L)	Response factors ($\times 10^9$)				
	2,4-DNT	TNT	RDX	4ADNT	2ADNT
1	1.14	1.13	0.748	0.789	0.832
0.5	1.93	1.83	1.05	1.07	1.14
0.25	2.82	2.48	1.27	1.31	1.39
0.1	4.37	3.84	1.56	1.42	1.46
0.05	5.31	4.78	1.70	1.35	1.41
0.025	6.17	5.08	1.75	1.49	1.39
0.01	7.29	5.64	1.86	ND*	ND

*Not measured by integrator.

Table 4. Response factors (HP integrator peak height divided by mg /L concentration) for RP-HPLC analysis, based on duplicate measurements.

Concentration (mg/L)	Response factors ($\times 10^9$)				
	2,4-DNT	TNT	RDX	4ADNT	2ADNT
10	11.8	16.3	13.6	4.11	6.16
5	11.5	15.8	13.3	4.30	6.02
1	11.9	16.0	13.7	4.19	6.34
0.5	11.8	16.4	13.7	4.14	6.35
0.25	11.6	16.3	13.0	4.37	6.02
Mean	11.7	16.1	13.5	4.22	6.18
Std. Dev.	0.16	0.29	0.30	0.110	0.163
RSD	1.37%	1.79%	2.25%	2.60%	2.64%

ear than that of the NPD for RDX, and likewise for the other target analytes, the NPD was deemed more practical for field applications. Moreover, the small nonlinearity for the NPD causes only a slight underestimation of the low analyte concentrations (less than 1 mg/L or mg/kg). For these reasons only the NPD detector was evaluated during the subsequent studies.

MDL tests

Table 5 shows the results of the soil MDL study for the target analytes at concentrations ranging between 0.39 and 0.51 mg/kg. The MDLs obtained from this study ranged from 0.087 mg/kg for 4ADNT to 0.15 mg/kg for 2,4-DNT, and recoveries ranged from 94.7 to 113%. Table 6 shows the MDL results for aqueous solutions spiked at concentrations ranging from 2.08 to 2.71 µg/L for the five target analytes. The MDLs for these aqueous samples ranged from 0.32 to 0.82 µg/L. The analyte recoveries by this method SPE were lower than expected (61% to 71%) and will require further investigation. Possible explanations for these low recoveries are (1) differences in performance

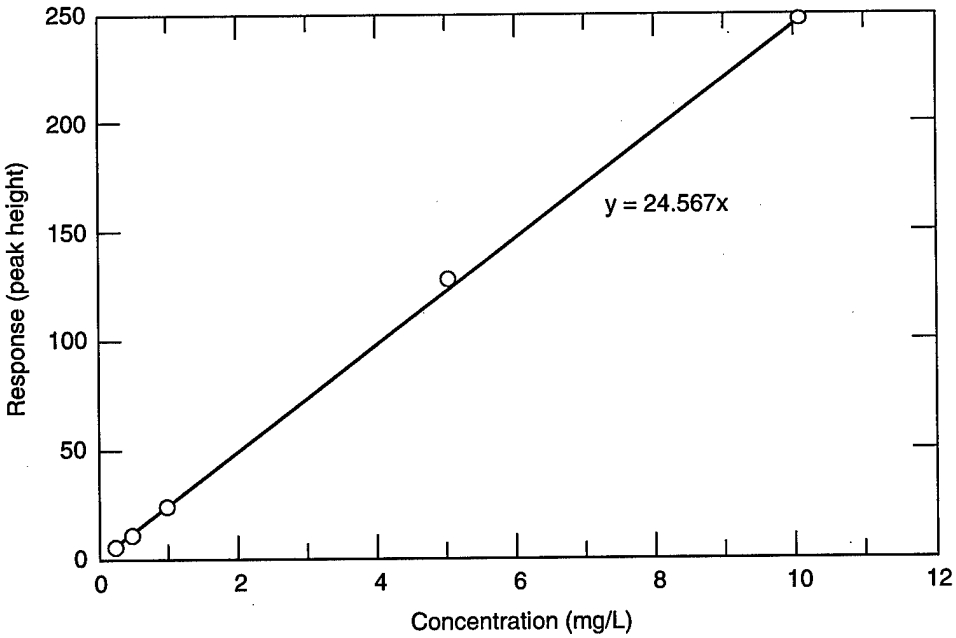

Figure 3. Calibration curve obtained for RDX by GC-NPD analysis.

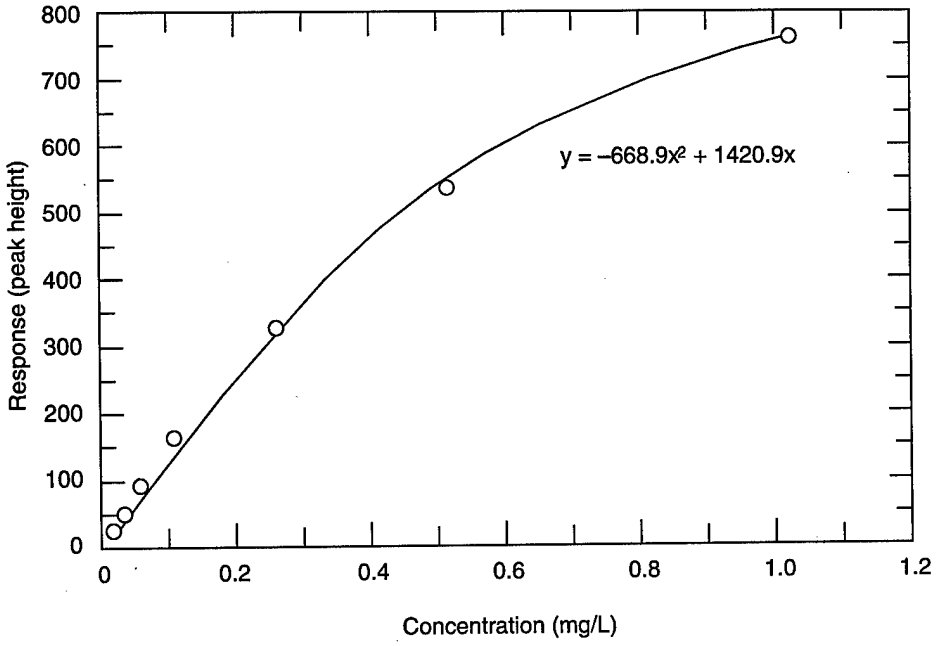

Figure 4. Calibration curve obtained for RDX by GC-ECD analysis.

Table 5. Method detection limit (MDL) study of blank soil spiked with five target analytes and analyzed by GC-NPD.

	Found concentration (mg/kg)				
Rep.	*2,4- DNT*	*TNT*	*RDX*	*4ADNT*	*2ADNT*
1	0.429	0.451	0.510	0.438	0.461
2	0.281	0.499	0.486	0.506	0.503
3	0.359	0.493	0.548	0.477	0.498
4	0.388	0.532	0.558	0.532	0.532
5	0.411	0.538	0.478	0.499	0.521
6	0.363	0.508	0.486	0.486	0.529
7	0.327	0.456	0.558	0.484	0.444
Theoretical*	0.386	0.497	0.505	0.454	0.442
Mean	0.365	0.497	0.518	0.489	0.498
Std. dev.	0.0505	0.0338	0.0361	0.0289	0.0340
MDL	0.15	0.10	0.11	0.087	0.10
Recovery	94.5%	100%	103%	108%	113%

*Expected analyte concentration.

Table 6. MDL study of 1-L reagent grade water samples fortified with five target analytes and analyzed by solid phase extraction and GC-NPD.

	Found concentration (µg/L)				
Rep.	*2,4-DNT*	*TNT*	*RDX*	*4ADNT*	*2ADNT*
1	1.55	2.11	2.08	2.33	1.83
2	1.66	1.98	1.73	1.91	1.57
3	1.88	2.16	1.82	2.11	1.74
4	1.61	1.74	1.72	1.82	1.51
5	1.67	1.82	2.02	1.68	1.42
6	1.65	1.91	1.91	1.66	1.43
7	1.74	1.68	2.08	2.27	1.88
Mean	1.68	1.91	1.91	1.97	1.63
Std. dev.	0.106	0.181	0.156	0.273	0.190
MDL	0.32	0.54	0.47	0.82	0.57

between batches of the extraction disks, or (2) a need to reduce the flow of the aqueous solutions through these membranes.

Comparison of results for GC-NPD vs. RP-HPLC for field-contaminated soils

A method comparison was performed by analyzing the same acetone extracts of field-contaminated soil samples by both RP-HPLC and GC-NPD. To obtain determinations for all of the analytes of interest, two RP-HPLC analyses were performed. With the exception of HMX, the compounds were quantified by RP-HPLC analysis using a C8 column. The RP-HPLC determination of HMX was performed using a CN column. The results in Table 7 show that there was usually very good agreement between these two methods of analysis, particularly for TNT and RDX. The highly significant correlation ($r^2 = 0.998$) between these instrumental methods for all explosive analytes is also shown in Figure 5. In a few cases, there was poor agreement between the methods and the failure of the GC-NPD analysis to identify a compound that was determined by RP-HPLC analysis. This occurred for 2ADNT and 4ADNT when HMX was present at some two to four orders of magnitude higher in concentration, and therefore they were not completely resolved

Table 7. Comparison between GC-NPD and RP-HPLC results for the solvent extracts of field-contaminated soil samples.

	Found concentration (mg/kg)					
Sample	*2,4-DNT GC / HPLC*	*TNT GC / HPLC*	*RDX GC / HPLC*	*4ADNT GC / HPLC*	*2ADNT GC / HPLC*	*HMX GC /HPLC*
E	BDL†/ 0.027	1.3 / 0.72	0.50 / 0.43	ND / 0.43	0.38 / 0.45	NQ / 3000†
F	BDL / 0.032	2.4 / 2.1	0.25 / 0.22	ND / 0.52	0.27 / 0.53	NQ / 2800†
K	BDL / 0.045	28† / 25†	0.48 / 0.30	0.52 / 0.39	ND / 0.31	NQ / 1500†
M	5.5 / 4.5	140† / 150†	13† / 10	ND / 0.34	ND / 0.43	ND / NA
N	1.3 / 2.0	250† / 300†	120† / 130†	ND / 1.4	ND / 3.5	ND / NA
O	2.5 / 2.8	440† / 540†	1.7 / 2.1	2.7 / 0.93	2.5 / 1.6	ND / NA
T	0.92 / 1.2	0.39 / 0.68	0.28 / 0.30	ND / 0.16	ND / 0.19	NQ / 1800†
U	1.6 / 1.7	0.43 / 0.28	0.10 / 0.085*	ND / 0.11	ND / 0.11	NQ / 1100

*Below GC-NPD detection level.
†Above calibration curve.
ND Not detected.
NA Not analyzed.
NQ Not quantitated.

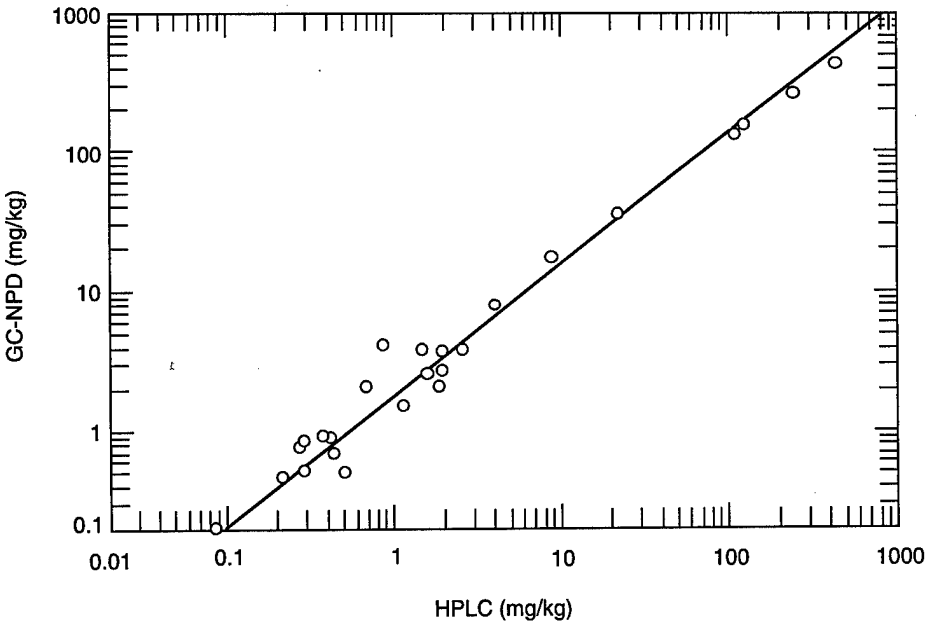

Figure 5. Comparison of target analyte concentrations (mg/kg) established by HPLC and GC-NPD analysis of field samples.

from this later eluting compound. On the other hand, excellent agreement between the methods was achieved for the determination or RDX at near-detection-limit concentrations even in the presence of high HMX concentrations.

Miscellaneous variables

The effect of soil moisture on GC-NPD response is shown in Table 8. TNT and 2,4-DNT do not appear to be significantly affected by moisture over the range tested, but the other three, less volatile, analytes show suppressed responses at the high soil moisture contents (> 30% by dry weight). Perhaps upgrading the detector with a heater would overcome this apparent suppression.

Table 9 shows that in addition to the five target analytes, several other compounds associated with the manufacturing and degradation of explosives can be detected by GC-NPD analysis. The only analytes not detected by the NPD were the ortho,

Table 8. Assessment of the effect of soil moisture on GC-NPD response.

	Percent average (n = 2) *response (pkht) relative to standard†*				
*Soil moisture**	*2,4-DNT*	*TNT*	*RDX*	*4ADNT*	*2ADNT*
5%	111	102	104	107	106
10%	102	100	96	104	100
20%	108	105	90	94	88
30%	102	98	81	89	84
40%	108	102	82	87	81
50%	105	100	72	83	77

*Dry weight basis.

†Responses were corrected for a proportional, volumetric dilution of acetone by water. These corrected responses were divided by the response obtained for a standard that did not contain water.

Table 9. Retention times for explosives using different oven temperature programs for NPD and ECD.

Analyte	*NPD retention time (min)*	*ECD retention time (min)*
NB	0.96	NA
o-NT	ND	NA
m-NT	ND	NA
p-NT	ND	NA
1,3-DNB	2.4	NA
2,6-DNT	2.6	NA
2,4-DNT	3.0	0.97
TNB	3.9	NA
TNT	4.1	1.7
RDX	4.7	2.7
4ADNT	5.3	4.2
2ADNT	5.6	5.1
Tetryl	6.1	NA
HMX	7.9	ND

NA Not analyzed.
ND Not detected at 10 mg/L concentration.

para and meta nitrotoluenes, which are among the least frequently encountered analytes found at sites contaminated with explosives. Therefore, this analytical method applies to most of the explosives cited by SW846 Method 8830, the standard laboratory method for explosives in water and soil.

An assessment of the upper range of the NPD's linearity was performed using the standards containing the five target analytes. This experiment showed that the response of the NPD remains linear up to 100 to 200 mg/L. Therefore, the range of linear response for these analytes is two to three orders of magnitude.

Lastly, no impurities were detected by GC-NPD analysis of hardware-store grade acetone. Furthermore, the analysis of a 1-mg/L standard of the target analytes prepared in both hardware-store and reagent-grade acetone resulted in identical responses. This finding would eliminate the need to ship large quantities of acetone to the field.

SUMMARY

These preliminary findings indicate that a robust and rapid field GC-NPD analytical method can be developed for the simultaneous identification and quantification of explosive residues in both soil and water matrices. When working with action levels for these analytes of 0.5 mg/kg and 2.0 µg/L, for soil and water, respectively, a field-transportable GC-NPD is a practical choice of instrumentation, even though lower levels of detection could probably be achieved by GC-ECD. The GC-NPD, coupled with the sample preparation methodologies described, offers the following features:

- Simultaneous determination of multiple target analytes,
- Adequate sensitivity,
- A linear range of response (except at concentrations less than 1 mg/L or 1 mg/kg) that exceeds current field screening technologies,
- Faster analytical runs than the currently recommended laboratory LC or GC methods,
- Compatibility with hardware-store grade acetone.

One of the only limitations of this methodology is that the instrumentation does require a fair amount of support. In addition to a source of electrical power, the NPD requires independent sources of both hydrogen and nitrogen gas.

Before recommending this methodology as an analytical approach for characterizing the extent and type of explosive contamination in soil and water, field trials need to be performed. Field verification would further establish the robustness of this analytical method and provide insight as to the number of samples that could be processed daily and better define the logistical requirements. Knowledge of all of these parameters is needed before estimates of cost saving can be made. Moreover, as with other methods based on chromatography, unanticipated interferences may be encountered during field studies.

This on-site method offers the potential to establish timely concentrations for individual explosives well above and below current action levels. Currently, this task cannot be unambiguously achieved using current on-site methodologies, since they either lack adequate sensitivity and/or the selectivity required. Therefore, this field analytical method could fulfill a very useful function in our effort to economically characterize active and formerly used manufacturing plants, ordnance works and disposal sites, depots, proving grounds, impact ranges, firing points, etc.

LITERATURE CITED

Bart, J.C., L.L. Judd, K.E. Hoffman, A.M. Wilkins, and A.W. Kusterbeck (1997) Application of a portable immunosensor to detect explosives TNT and RDX in groundwater samples. *Environmental Science Technology* **31**(5): 1505–1511.

Crockett, A.B., H.D. Craig, T.F. Jenkins, and W.E.

Sisk (1996) Field sampling and selecting on-site analytical methods for explosives in soil. Federal Facilities Forums Issue, EPA Report 540/R-97/501.

Crockett, A.B., T.F. Jenkins, H.D. Craig, and W.E. Sisk (1998) Overview of on-site analytical methods for explosives in soil. USA Cold Regions Research and Engineering Laboratory, Special Report 98-4.

Crockett, A.B., H.D. Craig, and T.F. Jenkins (in press) Field sampling and selecting on-site methods for explosives in water. EPA Federal Facilities Forum Issue paper. EPA Office of Research and Development, Office of Solid Waste and Emergency Response.

Erickson E.D., D.J. Knight, D.J. Burdick, and S.R. Greni (1984) Indicator tubes for the detection of explosives. Naval Weapons Center Report NWC TP 6569, China Lake, California.

Grant, C.L., T.F. Jenkins, and S.M. Golden (1993) Evaluation of pre-extraction analytical holding times for nitroaromatics and nitramine explosives in water. USA Cold Regions Research and Engineering Laboratory, Special Report 93-24.

Heller, C.A., S.R. Grenl, and E.E. Erickson (1982) Field detection of 2,4,6-trinitrotoluene in water by ion-exchange resins. *Analytical Chemistry*, **54:** 286-289.

Haas, R., and G. Stork (1989) Konzept zur Untersuchung von Rustungsaltlasten: 1. Untersuchung ehemaliger TNT-Fabriken und Fullstellen. *Fresenius Journal of Analytical Chemistry*, **335:** 839–846.

Haas, R., I. Schreiber, E. von Low, and G. Stork (1990) Conception for the investigation of contaminated munition plant wastes: 2. Investigation of former RDX-plants and filling stations. *Fresenius Journal of Analytical Chemistry*, **338:** 41–45.

Hutter, L., G. Teaney, and J.W. Stave (1993) A novel field screening system for TNT using EIA, p. 472 in *Field Screening Methods for Hazardous Wastes and Toxic Chemicals*, Vol. 1, *Proceedings of the 1993 U.S. EPA/A and WMA International Symposium.*

Jenkins, T.F. (1990) Development of a simplified field method for the determination of TNT in soil. USA Cold Regions Research and Engineering Laboratory, Special Report 90-38.

Jenkins, T.F., and P.W. Schumacher (1990) Evaluation of a field kit for detection of TNT in water and soils. USA Cold Regions Research and Engineering Laboratory, Special Report 90-20.

Jenkins, T.F., and M.E. Walsh (1992) Development of field screening methods for TNT, 2,4-DNT and RDX in soil. *Talanta*, **39:** 419–428.

Jenkins, T.F., and M.E. Walsh (1998) Reagent chemistry for on-site TNT/RDX determination. *Current Protocols in Analytical Chemistry*, John Wiley and Sons, V. Lopez-Avila, Ed., Unit 2D.2, 1998.

Jenkins, T.F., P.G. Thorne, and M.E. Walsh (1994) Field screening method for TNT and RDX in groundwater. USA Cold Regions Research and Engineering Laboratory, Special Report 94-14.

Jenkins, T.F., M.E. Walsh, P.G. Thorne, S. Thiboutot, G. Ampleman, T.A. Ranney, and C.L. Grant (1997) Assessment of sampling error associated with the collection and analysis of soil samples at a firing range contaminated with HMX. USA Cold Regions Research and Engineering Laboratory, Special Report 97-22.

Jenkins, T.F., M.E. Walsh, P.G. Thorne, P.H. Miyares, T.A. Ranney, C.L. Grant, and J. Esparza (1998). Site characterization at the inland firing range impact area at Ft. Ord. USA Cold Regions Research and Engineering Laboratory, Special Report 98-9.

Jian, C, and W.R. Seitz (1990) Membrane for in situ optical detection of organic nitro compounds based on fluorescence quenching. *Analytica Chimica Acta*, **237:** 265–271.

Keuchel, C., and R. Niessner (1994) Rapid field screening test for the determination of 2,4,6-trinitrotoluene in water and soil with immuno-filtration. *Fresenius Journal of Analytical Chemistry*, **350:** 538–543.

Keuchel, C., L. Weil, and R. Niessner (1992a) Effect of the variation of the length of the spacer in a competitive enzyme immunoassay (ELISA) for the determination of 2,4,6-trinitrotoluene (TNT). *Fresenius Journal of Analytical Chemistry*, **343:** 143.

Keuchel, C., L. Weil, and R. Niessner (1992b) Enzyme-linked immuno assay for the determination of 2,4,6-trinitrotoluene and related nitroaromatic compounds. *Analytical Sciences*, **8:** 9–12.

Shriver-Lake, L.C., K.A. Breslin, P.T. Charles, D.W. Conrad, J.P. Golden, and F.S. Ligler (1995) Detection of TNT using evanescent wave fiber-optic biosensor. *Analytical Chemistry*, **67:** 2431–2435.

Shriver-Lake, L.C, B.L. Donner, and F.S. Ligler (1997) On-site detection of TNT with a portable fiber optic biosensor. *Environ. Sci. Technol.* **31**(3): 837–841.

Stevanovic, S., and M. Mitrovic (1990) Colorimetric method for semiquantitative determination of nitroorganics in water. *International Journal of Environmental Analytical Chemistry*, **40:** 69–76.

Teaney, G.B., and R.T. Hudak (1994) Development of an enzyme immunoassay based field screening method for the detection of RDX in soil and water. *Proceedings of the 87th Annual Meeting and Ex-*

hibition, Air & Waste Management Association, Cincinnati, Ohio, 94-RP143.05.

Thorne, P.G., and T.F. Jenkins (1995) Development of a field method for ammonium picrate / picric acid in soil and water. USA Cold Regions Research and Engineering Laboratory, Special Report 95-20.

U.S. EPA (1997) Field analytical and site characterization technologies summary of applications. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response Technology Innovation Office, Washington, DC.

U.S. EPA (1989) Trinitrotoluene health advisory. U.S. Environmental Protection Agency, Office of Drinking Water, Washington, DC.

Walsh, M.E., and T.F. Jenkins (1991) Development of a field screening method for RDX in soil. USA Cold Regions Research and Engineering Laboratory, Special Report 91-7.

Walsh, M.E., and T.A. Ranney (1998) Determination of nitroaromatic, nitramine, and nitrate ester explosives in water using SPE and GC-ECD: Comparison with HPLC. USA Cold Regions Research and Engineering Laboratory, CRREL Report 98-2.

Walsh, M.E., T.F. Jenkins, P.S. Schnitker, J.W. Elwell, and M.H. Stutz (1993) Evaluation of analytical requirements associated with sites potentially contaminated with residues of high explosives. USA Cold Regions Research and Engineering Laboratory, CRREL Report 93-5.

Zhang, Y., and W.R. Seitz (1989) Single fiber absorption measurements for remote detection of 2,4,6-trinitrotoluene. *Analytica Chimica Acta,* **221:** 1–9.

Zhang, Y., W.R. Seitz, C.L. Grant and D.C. Sunberg (1989) A clean, amine-containing poly(vinyl)chloride membrane for in-situ optical detection of 2,4,6-trinitrotoluene. *Analytica Chimica Acta,* **217:** 217–227.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	August 1999	

4. TITLE AND SUBTITLE
On-Site Method for Measuring Nitroaromatic and Nitramine Explosives in Soil and Groundwater Using GC-NPD: Feasibility Study

5. FUNDING NUMBERS
WU: AF25-CT-006

6. AUTHORS
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army Cold Regions Research and Engineering Laboratory
72 Lyme Road
Hanover, New Hampshire 03755-1290

8. PERFORMING ORGANIZATION REPORT NUMBER
Special Report 99-9

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Environmental Center
Aberdeen Proving Ground
Maryland 21010-5401

Office of the Chief of Engineers
Washington, DC 20314-1000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
SFIM-AEC-ET-CR-99044

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.
Available from NTIS, Springfield, Virginia 22161

12b. DISTRIBUTION CODE

13. ABSTRACT (*Maximum 200 words*)

An on-site method has been developed for estimating concentrations of TNT, RDX, 2,4-DNT, and the two most commonly encountered environmental transformation products of TNT, 2-amino-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene, in soil and groundwater using gas chromatography and the nitrogen-phosphorus detector (NPD). Soil samples (20 g) are extracted by shaking with 20 mL of acetone, and extracts are filtered through a Millex SR (0.5-µm) filter. Groundwater samples (1 L) were passed through SDB-RPS extraction disks that were subsequently extracted with 5 mL of acetone. A 1-µL volume of a soil or water extract is manually injected into a field-transportable gas chromatograph equipped with a NPD and a heated injection port. Separations are conducted on a Restek Crossbond 100% dimethyl polysiloxane column, 6 m × 0.53-mm i.d., 1.5 mm, using nitrogen carrier gas at 9.5 mL/min. Retention times range from 3.0 min. for 2,4-dinitrotoluene (2,4-DNT) to 5.6 min. for 2-amino-4,6-dinitrotoluene. Method detection limits were less than 0.16 mg/kg for soil and less than 1.0 µg/L for groundwater. One of the major advantages of this method, over currently available colorimetric and enzyme immunoassay on-site methods, is the ability to quantify individual target analytes that often coexist in soils and groundwater contaminated with explosive residues. This method will be particularly useful at military antitank firing ranges where it is necessary to quantify residual concentrations of RDX in the presence of high concentrations of HMX, and when the transformation products of TNT need to be identified.

14. SUBJECT TERMS			15. NUMBER OF PAGES
	Explosives Gas chromatography Nitrogen-phosphorus detectors	On-site analysis TNT	22
			16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL